# I C A S E  R E P O R T

## SELECTION OF TERMS FOR A CI WAVEFUNCTION TO PRESERVE POTENTIAL SURFACE FEATURES

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# SELECTION OF TERMS FOR A CI WAVEFUNCTION TO PRESERVE POTENTIAL SURFACE FEATURES

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ABSTRACT

A cumulative selection procedure for choosing configuration functions for inclusion in CI calculations is described. The objective of the method is to obtain equal energy loss, relative to unselected calculations, for different states and different regions of the potential surface. Results obtained from calculations on the BH molecule indicate an overall advantage in comparison to the threshold selection procedure, particularly with regard to molecular geometry changes.

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## I. Introduction

It is well known that the method generally referred to as configuration interaction (CI) is capable in principle of producing accurate *ab initio* potential surfaces for both ground and excited states of molecular systems. Energies of excited states are obtained either as higher eigenvalues of the same matrix eigenvalue problem which is solved for the ground state, or from a separate eigenvalue problem (particularly for states of different symmetry). Computed surfaces depend only upon the quality of the expansion basis if the CI wavefunction is "full," which implies complete basis utilization. In practice, full CI wavefunctions are seldom employed because of the very large number of terms involved, and because it has been demonstrated [1] that if the orthonormal orbital basis is chosen carefully and if the wavefunction terms are limited to those which correspond to lower-level excitations (or particle-hole combinations), a large percentage of the full CI energy may be recovered. It is often found that even such excitation-limited CI (EL-CI) wavefunctions involve too many terms for practical calculation. (The computational effort is proportional to the square of the number of terms.) However it has been further demonstrated that a very large fraction of the EL-CI wavefunction terms make negligible contribution to the total energy and wavefunction [1-4], the actual fraction depending largely on the orbital basis [5,6]. This note describes a procedure for the identification and selection of the important terms of an EL-CI wavefunction in such a way that the resulting selected EL-CI (SEL-CI) computed potential surfaces will faithfully reproduce the shape of the EL-CI potential energy surface by being as nearly parallel to it as practical. Furthermore, the procedure is designed for the computation of potential surfaces for several states of a molecular system such that their relative positions are faithfully reproduced.

An important criterion for the design of this procedure is to minimize user intervention and user bias in its application, making its operation as automatic as possible.

The basic philosophy of this approach can be summarized as follows: Rather than asking which terms need be included to get the important energy-lowering effects, the question is asked, "which terms may be rejected, with a consequent raising of the energy, while meeting the primary objective of calculating potential curves which are parallel to, and equally displaced from, the curves of unselected calculations?" The change in point of view is important as regards the requirement of a correct surface characterization. A molecular electronic system may undergo drastic changes when the nuclei are disturbed. For example, consider the dissociation of a molecule into fragments: electron pairs (bonds) are broken, other electrons may pair up, and electrons may recouple their spins. The simplest realization of the Hartree-Fock orbital model (the single determinant) is not generally capable of describing the complicated electron behavior, but nevertheless it usually provides the zeroth-order term of a CI wavefunction. However, in dissociative regions the CI energy gain (the correlation energy) is larger than that in the bonding region. It is evident that in general the energy gain cannot be considered even nearly constant over the surface. While a carefully constructed EL-CI wavefunction would presumably produce the necessary energy gain in all regions, many negligible terms will usually be contained in it. It seems clear that raising the EL-CI energy a small constant increment, by rejecting terms with small contributions, is more likely to meet the primary objective than lowering the zero-order energy an undetermined and possibly large increment by adding selected terms to the zeroth-order (SCF) wavefunction.

Figure 1 displays the idea of the method schematically. The curve labeled A represents the result of an EL-CI computation, which is assumed to be above and parallel to a true potential curve (not shown). The curve labeled C is characteristic of a limited orbital self-consistent field approach and we wish to compute a curve between A and C such as that labeled B. The objective is to get B parallel to A, with a relatively small and known vertical separation between B and A; the vertical separation between B and C is variable, large, and generally unknown. It will be shown how this approach can be used to compute curves like B not only for ground states but also for excited states.

## II. The Selection Procedure

### A. Theory

A general accurate CI wavefunction expansion can be viewed as consisting of the linear combination,

$$\Psi = C_P\Psi_P + C_S\Psi_S + C_R\Psi_R \ , \tag{1}$$

where

$$\Psi_Q = \sum_{q \in Q} c_q \Phi_q \quad , \ (Q \equiv P, S, \text{ or } R) \ . \tag{2}$$

The letters P, S, and R represent principal, selected, and rejected, and $\Phi_q$ is a spin-adapted configuration function (CF). We assume the existence of a quantity $\delta E_q$ which measures the effect of the term $\Phi_q$ on the total variation energy $E[\Psi]$ of the system,

$$E[\Psi] = \langle\Psi|\hat{H}|\Psi\rangle/\langle\Psi|\Psi\rangle \ , \tag{3}$$

where $\hat{H}$ is the molecular hamiltonian. We further assume that the energy

contributions $\delta E_q$ are additive, particularly for the less important terms of R, so that

$$E[\Psi] \simeq E[\Psi_{PS}] + \sum_r \delta E_r \ , \tag{4}$$

where $\Psi_{PS}$ represents the wavefunction (1) truncated to include only the terms of P and S. If for all geometries and for each potential surface the sum in equation (4) is maintained constant by a suitable choice for the set R, then the primary objective is met: the energy $E[\Psi_{PS}]$ is the energy for a parallel displaced potential surface and is computed from the wavefunction $\Psi = \Psi_{PS}$. This can be accomplished by choosing a threshold $\sigma$ which is applied to the summation in (4), rather than applying a selection threshold to each individual term in S and R (SR). This summation threshold should then be nearly equal to the energy lost in truncating $\Psi$ to terms in P and S by the selection. To be consistent, the procedure must produce disjoint sets S and R such that

$$|\delta E_s| > |\delta E_r| \ , \tag{5}$$

for all $r \in R$ and $s \in S$. The following discussion describes the procedures of the cumulative selection method more fully, giving the extension for the treatment of several states.

B. The EL-CI Wavefunction

An EL-CI wavefunction consists classically of the Hartree-Fock CF plus others generated from the basic Hartree orbital product by excitation of electrons from occupied to virtual orbitals of the Hartree-Fock-Roothaan manifold, by multiplication with appropriate spin functions, and finally by antisymmetrization. An EL-CI wavefunction can be characterized by the largest number of electrons promoted to the virtual space. As the maximum

excitation level increases, the allowed number of orbital products increases rapidly, so that it is desirable for practical reasons to keep the excitation level as low as possible. While the double-excitation level usually leads to an EL-CI wavefunction of reasonable size, it is known that certain higher excitations (particularly quadruple-excitations) can make significant variational contribution to the energy [7]. For most interesting molecular systems it is generally quite impractical to include all quadruple-excitation CF's even prior to an efficient selection process. It is possible however to include limited numbers of higher excitation CF's by use of a straightforward generalization of the wavefunction form. If the zeroth-order wavefunction contains certain important double (and perhaps single) excitation terms in addition to the Hartree-Fock CF, then a consistent level of excitation with respect to each term will necessarily produce certain higher excitation species (relative to Hartree-Fock) in the EL-CI wavefunction [8,9]. This device has been discussed in detail by Buenker and Peyerimhoff [9] in a recent paper in which extensive supporting data is given. It is with this EL-CI wavefunction structure in mind that the wavefunction has been expressed in the form of equation (1), consisting of principal (P) and secondary (SR) terms.

We concur in general with the contention of Buenker and Peyerimhoff [9] that if several highly important terms are included in the P set and if the SR set consists of terms which are no higher in excitation-level than double with respect to at least one term in P, then the resulting EL-CI wavefunction can give a very good description of the system, including some of its excited states and corresponding potential surfaces. For this purpose the principal set P should include all terms required for the correct description of dissociation and any others which are found in sub-

sequent tests to make substantial contributions to the wavefunction at any point on the surface.

It is useful to consider the generalized EL-CI wavefunction as arising from excitations from an internal set of orbitals to an external set [8]. It is of course clear that the usual second-order energy contribution formulas for CF's, computed relative to $\Psi_P$ as the zero-order function, cannot measure the effect of higher than double excitations relative to all the terms in the principal set [9].

C. Additivity of Energy Contributions

Relation (4) has been derived and discussed in detail by Bunge [10] and by Buenker and Peyerimhoff [9]. For appropriate energy contributions of the type discussed below, it is an approximate relation which depends on the fact that R represents terms $\Phi_r$ which contribute little to the total energy and which interact weakly with terms of P and S. The extent to which the relation is an accurate description of the exact energy (for given $\Psi$) will depend on the reliability of the $\delta E_r$ and on the choice of a suitable summation threshold value by which the S-R separation is established. As an approximation, relation (4) is useful as long as its approximate nature does not change severely for widely separate points of a potential surface. The extent of its validity can only be determined by empirical tests.

D. Several States

The discussion above does not address the "several state" aspect of the primary objective. The extension to the case of states of different symmetry is straightforward. For each SEL-CI potential curve to parallel its EL-CI counterpart with equal vertical displacement , the summation threshold $\sigma$ is chosen the same for the different states. To the extent that this summation threshold equals the actual energy loss, the objective

is met. At the same time, it is assumed that the EL-CI master lists for the different states are reasonably equivalent in terms of approximating full-CI results. This places considerable demands on the choices of the orbital set and of the terms included in $\Psi_P$ in each case, so as to avoid bias in favor of any particular state.

The approach for several states of the same symmetry is not so straightforward, and at least two different schemes may be used. The first begins with a choice of a set P which includes the important CF's for all of the states to be determined simultaneously. Following this, a master list of CF's is generated in the same EL-CI form as for a single state. Since P now contains more terms, so will the master list. At this point energy contributions are computed for each term in the master list relative to each of the states. The threshold $\sigma$ is then used to select terms by summation of the separate energy contribution lists of the different states, and to define separate SEL-CI lists, each of which contains the P set. The set R is then obtained as the union of all the terms selected for the individual states. The Hamiltonian matrix is computed, and as many of the lowest eigenvalues and corresponding eigenvectors as are of interest are obtained. This approach must introduce additional error, as regards the objective of a equivalent energy loss for all states, because the independent SEL-CI lists will in general have terms which are not in common and which consequently will contribute to lowering the energy of the other states. It is hoped that the additional error is not greater than the other errors in the proposed procedure, and the results obtained for just two states seem to bear this out.

An alternative approach would involve setting up separate hamiltonian matrices for each state, using the separate SEL-CI lists each

containing common P terms, and obtaining the relevant eigenvalue and eigenfunction of each. In this way the orthogonality of states would be only approximate and would depend on the actual summation threshold $\sigma$. Since larger absolute error may be acceptable in the computation of the transition moments than of the energy, the likely small nonorthogonality may not be a real deterrent to the use of this latter procedure.

## III. Algorithms

The basic algorithm for carrying out the cumulative selection on a computer is rather simple. First the master configuration list for an EL-CI wavefunction is set up. Secondly the energy contributions are computed for all terms of the SR set. Next the absolute values of the energy contributions are sorted into ascending order, keeping track of the term numbers. The absolute values of the energy contributions are then added up in order, beginning with the smallest, until the value of $\sigma$ is exceeded by the addition of one more term. All terms corresponding to the summed energy contributions are deleted from the EL-CI master list, leaving the SEL-CI list. Finally the variational energy and wavefunction are computed using this SEL-CI list.

The size limitation of computer memory and the need to treat very large EL-CI wavefunctions requires efficient coding practice. Before sorting a very long list of N items (an N log N process), it is worthwhile to cull the list by deleting at least those contributions whose value is extremely small (e.g. less than the accuracy of the integrals) and also those whose value is greater than some large fraction of $\sigma$. The former are relegated to R while the latter must belong to S. We keep track of selected terms using an array which contains one bit per EL-CI master list term. These

bits are set to "off" at the start, and are later turned "on" for the selected terms. The union of SEL-CI term lists for multiple states is easily accomplished by the "logical or" operation. This compact storage of the selection information makes possible the in-core handling of very large EL-CI master lists.

## IV. Energy Contributions

The energy contributions $\delta E_q$ are measures or estimates of the ability of each wavefunction term $\Phi_q$ to change the total molecular energy by its addition to (or removal from) $\Psi$. Estimates of $\delta E_q$ are usually obtained from approximate CI calculations or perturbation-like evaluations of $\Psi$. Various expressions for $\delta E_q$ have appeared in the literature [2-4, 6, 9-12], and in the examples included in this work we compare two choices which are obtained in connection with the "$A_k$" and "$B_k$" procedures of Gershgorn and Shavitt [11]. In each case, consistent with our aims, the $k$ set is taken to be the set $P$ of principal CF's. By the $A_k$ prescription, the quantity $\delta E_q$ is defined to be the energy lowering obtained by adding the single term $\Phi_q \in SR$ to $P$ so that

$$\delta E_q = E[\Psi_P] - E[\Psi_{P\cup q}] \tag{6}$$

where $\Psi_P$ is defined in (2) and

$$\Psi_{P\cup q} = C_P\Psi_P + C_q\Phi_q \ , \ q\in SR \ , \tag{7}$$

the coefficients $c_p$ in (2) being fixed by a one-time variational determination of

$$E[\Psi_P] = \langle\Psi_P|\hat{H}|\Psi_P\rangle/\langle\Psi_P|\Psi_P\rangle \ . \tag{8}$$

This $\delta E_q$ is then equal to the second-order energy contribution of $\Phi_q$ relative to $\Psi_P$ as the zero-order function.

In the $B_k$ prescription, the $\delta E_q$ values are obtained simultaneously for all terms in SR by the approximate solution of the variational problem in the total PSR space, the approximation arising from the neglect of matrix elements $H_{qr}$ for which $q \neq r$ and $q$, $r$ are both in SR. The actual energy contribution of $\Phi_q$ may be estimated from the expression

$$\delta E_q = E[\Psi_{PSR-q}] - E[\Psi_{PSR}] , \tag{9}$$

where the coefficients of terms in $\Psi_{PSR-q}$ (which represents the full wavefunction expansion $\Psi_{PSR}$ less the $q^{th}$ term) are assumed to be the same as in $\Psi_{PSR}$. This leads to the formula [12]

$$\delta E_q = c_q^2 (H_{qq} - E[\Psi_{PSR}])/(1 - c_q^2) , \tag{10}$$

and the coefficients $c_q$ and energy $E[\Psi_{PSR}]$ are conveniently obtained from the $B_k$ approximation.

While other formulas for $\delta E_q$ could be used, it is believed that the proposed procedure will produce sufficiently representative results, and will allow critical tests of the overall selection scheme.

Values for $\delta E_q$ obtained from both the $A_k$ and $B_k$ procedures have been used in the usual threshold selection method (vide infra) and in the proposed cumulative selection scheme to see if any significant differences exist. For selection from very large EL-CI master lists it is computationally easier to use the $A_k$ procedure which handles the CF's in SR one at a time and thus requires only a small amount of machine resources, independently of the size of the master list. Test calculations were carried out on several states of the BH molecule as a function of the internuclear

distance R, since unselected EL-CI results were available for comparison [13]. Results (i.e. numbers of CF's selected) comparing four selection methods for two $^3\Sigma^+$ states are shown in table I. While it is not evident from the table, it is found that the sets of terms selected using $A_k$ and $B_k$ in each respective case are quite similar. Evidently the differences between $A_k$ and $B_k$ energy contributions must be small. Results which follow herein have all be obtained using $A_k$-type energy contributions.

## V. Other Selection Methods

We have compared our procedure to the frequently used threshold selection procedure [2,4]. In that scheme an absolute threshold $\tau$ is chosen, and all CF's which have energy contributions whose absolute value individually exceeds the threshold are retained. While the absolute threshold $\tau$ is basically different from $\sigma$, the EL-CI master list of CF's is used as a common starting point. This method is usually effective for calculations of molecular ground states near their equilibrium geometries. If no drastic changes in electronic structure are brought about by displacement of the nuclei, nearly constant energy contributions may be expected, and nearly equal selection errors (and selected CF lists) will be obtained. With large geometry change, however, substantial reorganization of the electrons is likely and the threshold selection procedure will fail to meet the objective. For different states (of the same or different symmetry) a different number of terms is likely to be selected, and the sum of rejected energy contributions may vary considerably. Hence vertical spectra so computed are anticipated to be poorer than those obtained by the cumulative selection method.

One interesting application of threshold selection to lowest state potential curves is that of Bagus et al. [14] on BeH. These authors found

the process to be unsatisfactory because a hump in the ground state curve relative to the full (unselected) three-electron CI wavefunction persisted for all nonzero values of $\tau$ employed ($5\ \mu h \leq \tau \leq 100\ \mu h$). Their result may be partly due to their unusual choice of the virtual or external orbital manifold. (If all terms of an EL-CI wavefunction are used, an orthonormal transformation among the external orbitals cannot affect the energy [6,8], but this no longer holds if selection is used; an appropriate choice of the virtual orbitals may be necessary for the success of the method, and is desirable for the purpose of obtaining a compact wavefunction.

More recently Buenker and Peyerimhoff [9,15] have recommended using threshold selection for a monotone sequence of $\tau$ values, accompanied by extrapolation to $\tau = 0$. This procedure appears to be an excellent means for achieving precise estimates of energies for very large CI expansions. While the additional work needed to obtain the several energies may be inconvenient when a full surface, consisting of many points, is to be computed, it is not excessive. The extrapolation procedure can make very good use of the extensive intermediate computations, and the entire procedure can be carried out automatically and efficiently. Of course, the proposed cumulatively selected energies can also be extrapolated with respect to a sequence of $\sigma$'s. It appears likely, in fact, that a $\sigma$-sequence extrapolation would be more accurate than one based on the $\tau$ sequence, because $\sigma$ represents a better measure of the energy error than can be obtained from $\tau$.

## VI. Results

In order to assess the performance of the basic cumulative selection method we first show results obtained in computations of a single potential

curve for the BH $X\,^1\Sigma^+$ ground state. A twenty-four orbital basis (determined from SCF calculations for the $^3\Sigma^+$ state), ten principal terms and the frozen-core approximation for the $1\sigma$ electrons give rise to 1292 spin and symmetry adapted CF's, an EL-CI master list which is small enough so that a variational solution is quite easily obtained. Table II presents the number of selected PS terms N, the quantity $\delta E_N$, which is the energy contribution of smallest magnitude included in the N selected terms, and $\Delta E$, the actual energy loss suffered, obtained as the difference between the variational energies $E[\Psi]$ and $E[\Psi_{PS}]$. If relation (4) were an exact equality we should expect all values of $\Delta E$ to be equal to the corresponding value of $\sigma$. In fact, appreciable variation in $\Delta E$ vs. R is observed, although it is substantially less than an order of magnitude. The equivalence of $\Delta E$ to $\sigma$ is less satisfactory, in particular for smaller $\sigma$, but such equivalence is not strictly required if a proportionality is maintained. We note in particular the strong variation in $\delta E_N$ vs. R. That variation is always found to be such that if the threshold selection procedure were applied instead, the consequent variation in $\Delta E$ vs. R would be larger because more configuration functions would be selected at large R. This point is demonstrated quite effectively in the comparisons described below.

Turning now to multistate calculations, tables III and IV display the results of the application of both threshold and cumulative selection to the two lowest $^1\Sigma^+$ and $^3\Sigma^+$ states of BH. The full details of these calculations will be given in [13], and it is sufficient for this work to say that all calculation parameters (basis set, orbital derivation, etc.) are held constant throughout each table. For the $i^{th}$ eigenvalue (or the $i^{th}$ state of either symmetry), the numbers ($N_i$) of CF's selected and the

actual energy losses ($\Delta E_i$) with respect to unselected EL-CI wavefunctions are tabulated for several internuclear distances R. Eigensolutions for both selection procedures are obtained from common ("merged set") hamiltonian matrices of dimension N corresponding to the union of the $N_1$ and $N_2$ lists. Specific values of $\tau$ and $\sigma$ were chosen to allow a comparison of the two separate methods, even though these parameters are inherently of different character.

The data in tables III and IV demonstrate behavior similar to that observed in table II as regards agreement of $\sigma$ and $\Delta E_i$. As was predicted for the case of a single state, the undesirable variation of $\Delta E_i$ vs. R is larger in most cases when threshold selection is employed. In extreme cases the variation is as great as an order of magnitude (Table IV, $\tau$ = 10μh). A survey of all cases shows that $\Delta E_1$ and $\Delta E_2$ agree better in the cumulative selection data, even though merged CF sets have been used.

The orbitals employed for the construction of the CF's were the SCF orbitals determined for the lowest state of each symmetry species. It had been suspected that when multiple states are computed, such a choice will bias the CI results in favor of the lowest state (i.e. the lowest state will have lower selection errors than the excited state). This is confirmed by the results in tables III and IV. It is also seen that $\Delta E_1$ and $\Delta E_2$ agree better for the $^3\Sigma^+$ states than for the $^1\Sigma^+$ states. It appears that the ground state SCF orbitals are a poorer choice for the $2^1\Sigma^+$ state than are the $1^3\Sigma^+$ orbitals for the $2^3\Sigma^+$ state; this is reflected by the fact that $N_2 > N_1$ consistently for the singlets, but not for the triplets, and affects the relative accuracy of the selected CI results.

## VII. Summary

A cumulative selection procedure has been presented for the balanced selection of important CF's from long lists of CF's generated by a straight-

forward CI technique. The reduction in size of the associated hamiltonian matrices makes possible the use of CI methods for a wider class of important chemical problems. The procedure is designed to produce a nearly parallel and constant displacement of potential curves relative to unselected calculations and to reproduce the relative positions of potential curves for different electronic states. Numerical results show the superiority of this approach over the commonly used threshold selection procedure. The performance of the proposed method depends to some extent on the appropriate choice of the orbitals used to construct the configuration functions. Its ability to represent true potential curves also depends, obviously, on the adequacy of the original, unselected, master list of CF's, on the underlying basis set, and on the choice of the orthonormal orbitals used to construct the CF's.

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Table I. Comparison of "$A_k$" and "$B_k$" energy contributions: Numbers of configurations selected for the lowest two roots of the BH $^3\Sigma^+$ state.[a,b]

| R | Threshold Selection | | | | Cumulative Selection | | | |
|---|---|---|---|---|---|---|---|---|
| | 100 μh | | 10 μh | | 5000 μh | | 500 μh | |
| | $A_k$ | $B_k$ | $A_k$ | $B_k$ | $A_k$ | $B_k$ | $A_k$ | $B_k$ |
| 1.800 | 111 | 108 | 290 | 290 | 102 | 102 | 335 | 335 |
| 2.336 | 125 | 120 | 321 | 321 | 119 | 119 | 339 | 345 |
| 3.000 | 149 | 148 | 384 | 377 | 180 | 172 | 453 | 438 |
| 3.500 | 122 | 122 | 341 | 331 | 138 | 133 | 417 | 398 |
| 5.000 | 83 | 84 | 226 | 223 | 73 | 69 | 262 | 252 |
| 13.000 | 66 | 65 | 126 | 123 | 39 | 38 | 93 | 92 |

[a] The master list for these states consists of 1122 symmetry-adapted configuration functions. The principal set consists of four dominant functions plus all single excitations, for a total of k = 21.

[b] Thresholds are given in units of $10^{-6}$ hartree (μh); distances (R) are in bohr.

Table II. Comparison of different cumulative selection thresholds as applied to the $X^1\Sigma^+$ ground state of BH.[a,b]

| R | σ = 5000 μh | | | σ = 500 μh | | | σ = 50 μh | | |
|---|---|---|---|---|---|---|---|---|---|
| | N | $\delta E_N$ | ΔE | N | $\delta E_N$ | ΔE | N | $\delta E_N$ | ΔE |
| 2.000 | 125 | 59 | 6817 | 371 | 4.1 | 1805 | 629 | .51 | 628 |
| 2.336 | 121 | 61 | 7705 | 353 | 4.9 | 2015 | 600 | .49 | 1025 |
| 2.600 | 120 | 71 | 8294 | 337 | 5.2 | 2331 | 566 | .51 | 743 |
| 4.000 | 84 | 107 | 7256 | 230 | 6.7 | 1995 | 437 | .45 | 610 |
| 5.000 | 56 | 111 | 7359 | 193 | 7.5 | 1276 | 363 | .70 | 403 |
| 13.000 | 25 | 485 | 5077 | 49 | 60.9 | 711 | 62 | 12.40 | 268 |

[a]The master configuration list for this state consists of 1292 spin-adapted configuration functions. The principal set included 10 dominant functions.

[b]Energies are in units of $10^{-6}$ hartree (μh); distances are in bohr.

Table III. Comparison of threshold and cumulative selection procedures as applied to the two lowest $^1\Sigma^+$ states of BH.[a,b]

| R | Threshold Selection | | | | | Cumulative Selection | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | N | $N_1$ | $\Delta E_1$ | $N_2$ | $\Delta E_2$ | N | $N_1$ | $\Delta E_1$ | $N_2$ | $\Delta E_2$ |
| | $\tau$ = 10 μh | | | | | $\sigma$ = 500 μh | | | | |
| 2.000 | 324 | 176 | 1160 | 228 | 2619 | 358 | 185 | 1070 | 273 | 2171 |
| 2.336 | 322 | 168 | 1318 | 232 | 2709 | 376 | 193 | 996 | 280 | 1984 |
| 2.600 | 328 | 177 | 1322 | 230 | 2630 | 388 | 199 | 889 | 292 | 1645 |
| 3.500 | 331 | 174 | 1137 | 234 | 2705 | 399 | 199 | 841 | 301 | 1664 |
| 5.500 | 238 | 134 | 1564 | 179 | 2237 | 276 | 135 | 1500 | 227 | 1684 |
| 10.000 | 130 | 55 | 1479 | 81 | 1436 | 106 | 42 | 2092 | 68 | 1799 |
| | $\tau$ = 100 μh | | | | | $\sigma$ = 5000 μh | | | | |
| 2.000 | 141 | 72 | 5107 | 90 | 7676 | 142 | 66 | 5740 | 96 | 7343 |
| 2.336 | 137 | 68 | 5658 | 88 | 7981 | 146 | 67 | 5982 | 100 | 7202 |
| 2.600 | 145 | 71 | 5399 | 93 | 7379 | 151 | 68 | 5689 | 102 | 6993 |
| 3.500 | 133 | 64 | 5833 | 86 | 8889 | 141 | 60 | 5919 | 98 | 8281 |
| 5.500 | 109 | 46 | 3915 | 80 | 7089 | 95 | 38 | 4734 | 69 | 8613 |
| 10.000 | 76 | 36 | 2372 | 41 | 3004 | 45 | 20 | 4768 | 25 | 6314 |

[a] The master configuration list for this case consists of 1267 spin-adapted configuration functions. The principal set includes 19 dominant functions.

[b] Energies are in units of $10^{-6}$ hartree (μh); distances are in bohr.

Table IV. Comparison of threshold and cumulative selection procedures as applied to the two lowest $^3\Sigma^+$ states of BH.[a,b]

| R | Threshold Selection | | | | | Cummulative Selection | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | N | $N_1$ | $\Delta E_1$ | $N_2$ | $\Delta E_2$ | N | $N_1$ | $\Delta E_1$ | $N_2$ | $\Delta E_2$ |
| | | $\tau$ = 10 μh | | | | | $\sigma$ = 500 μh | | | |
| 1.800 | 290 | 169 | 1121 | 152 | 1096 | 335 | 194 | 860 | 183 | 795 |
| 2.336 | 321 | 191 | 1492 | 179 | 1081 | 339 | 206 | 1397 | 197 | 926 |
| 3.000 | 384 | 265 | 1098 | 257 | 1473 | 453 | 314 | 717 | 324 | 867 |
| 3.500 | 341 | 222 | 994 | 205 | 1353 | 417 | 269 | 602 | 258 | 877 |
| 5.000 | 226 | 138 | 669 | 132 | 1234 | 262 | 161 | 539 | 162 | 890 |
| 13.000 | 126 | 74 | 152 | 52 | 969 | 93 | 55 | 628 | 38 | 1568 |
| | | $\tau$ = 100 μh | | | | | $\sigma$ = 5000 μh | | | |
| 1.800 | 111 | 60 | 5103 | 54 | 4633 | 102 | 57 | 5403 | 48 | 5333 |
| 2.336 | 125 | 71 | 5760 | 63 | 5191 | 119 | 68 | 6075 | 58 | 5550 |
| 3.000 | 149 | 92 | 6327 | 94 | 6779 | 180 | 118 | 4929 | 115 | 5326 |
| 3.500 | 122 | 71 | 6029 | 75 | 6064 | 138 | 86 | 4922 | 80 | 5636 |
| 5.000 | 83 | 39 | 4066 | 49 | 4040 | 73 | 36 | 4436 | 40 | 5333 |
| 13.000 | 66 | 35 | 2260 | 31 | 1876 | 39 | 20 | 4974 | 19 | 5267 |

[a] The master configuration list for this case consists of 1122 spin-adapted configuration functions. The principal set includes 4 dominant functions and single excitations for a total of 21.

[b] Energies are in units of $10^{-6}$ hartree (μh); distances are in bohr.

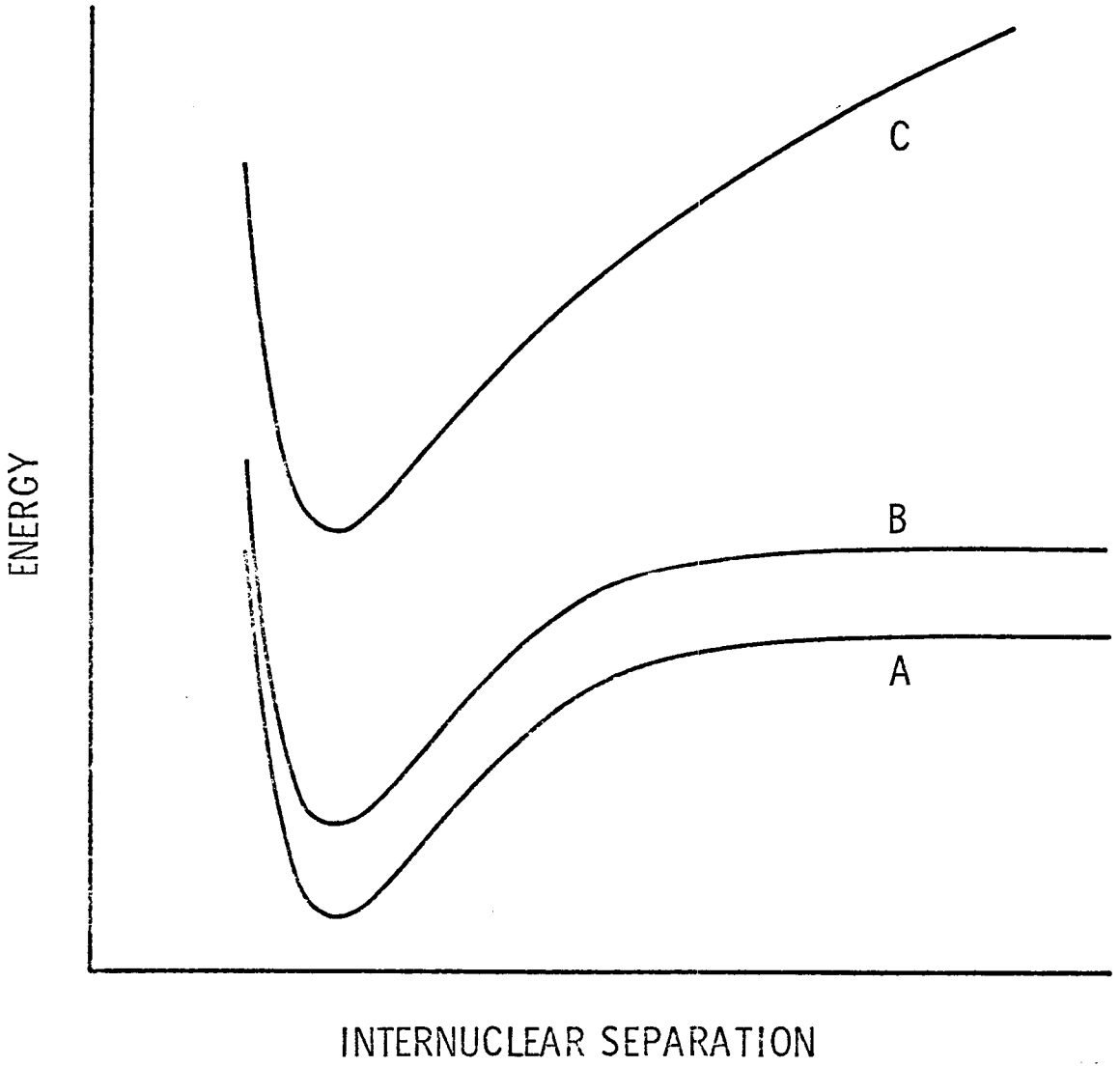


FIGURE 1: Schematic representation of the configuration selection approach to potential curve calculation. A. Result of EL-CI (unselected) calculation. B. Result of selected (SEL-CI) calculation. C. Zero-order curve (such as SCF).